

PATENT SPECIFICATION

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(54) CONTINUOUS PROCESS FOR CARRYING OUT A REACTION IN A BUBBLE COLUMN REACTOR

- (71) We, SCHERING AKTIEN-GESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 The invention relates to a continuous process for carrying out a physical or chemical reaction.
- 15 German Patentschrift No. 1,028,096 discloses an attempt, by the insertion in flow-through reactors of sieve plates, of which the perforations must be less than 1 mm in diameter, to produce gas cushions beneath the sieve plates. However, that specification does not give sufficient directions to ensure the reproducible formation of gas cushions.
- 20 The present invention provides a continuous process, which may be used for carrying out a physical or, preferably, a chemical reaction, which process comprises passing a liquid and a gas upwards through a reactor which includes a number of perforated plates, which plates are positioned across the direction of flow of the liquid and gas and divide the reactor into a number of individual sections, the reactor being so constructed that
- 30 (a) the ratio of the total perforation area of each perforated plate to the reactor cross-section in the vicinity of that plate is at most 15%, preferably at most 5%, and
- 35 (b) there is a fluid-impervious seal (as hereinafter defined) between each perforated plate and the reactor wall and
- 40 (c) each perforated plate is horizontal, and
- (d) each perforation in each perforated plate is the same size as the other perforations in that plate and the perforations are uniformly distributed over the plate, and
- 45 (e) each perforation either has a cylindrical or bevelled inlet, or is frustoconical with a wider inlet than outlet, and
- (f) the perforated plates are evenly spaced along the reactor and the distance between each pair of adjacent perforated plates is greater than three times the diameter of the reactor,
- 50 and the rates of flow of the liquid and the gas through the reactor being such that return of liquid and/or gas from one of the individual reactor sections to the preceding section is substantially, preferably completely, prevented.
- 55 By a "fluid-impervious" seal is meant a seal such that liquid is prevented from passing between the perforated plate and the reactor wall when the reactor is being used in the process of the invention. For convenience in manufacture, the various perforated plates are preferably identical to one another; in this case the size and distribution of the perforations will not vary from plate to plate.
- 60 Many different types of reactions can be carried out by the process of the invention. For example, the liquid may be reacted with the gas. Alternatively, the liquid may comprise two different chemical substances, each of which is in the liquid phase, and these two substances may react together in the presence of the gas. Furthermore, the liquid may contain in suspension a finely divided solid, the proportion of the solid preferably being at most 15% by weight, calculated on the weight of the liquid. When a solid is present, the liquid may react with the solid in the presence of the gas, or the liquid may react with the solid and with the gas.
- 65 Instead of containing in suspension a finely divided solid which reacts with the gas or the liquid, or both, the liquid may contain a finely divided solid which has a catalytic action on a chemical reaction. The proportion of the catalyst is preferably at most 20% by weight, calculated on the weight of the liquid.
- 70 With geometrical dimensions of reactor and perforated plates and flow rates of gas,
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liquid or suspension in accordance with the invention, axial back-mixing of the fluids between the individual reactor sections formed by the perforated plates is reduced or will be completely prevented if stable gas cushions are formed beneath the perforated plates. In the following description, this flow state is known as the "special flow state."

By the high throughput of gas and the continual redispersion of gas at the perforated plates the liquid and gas are turbulently mixed in the reactor sections and a high rate of mass transfer is thereby achieved. If the gas throughput is decreased to below the minimum value necessary for cushion formation the rate of mass transfer is reduced, but even with a reduction of the gas throughput to 50% of the minimum value for cushion formation back-mixing between the sections is still prevented to a sufficient extent. The lower rate of mass transfer has no influence in the case of reactions determined by reaction speed.

The invention also provides a reactor for carrying out the process of the invention. The reactor comprises a reaction tube and a number of perforated plates positioned across the tube to divide the tube into a number of individual sections, the reactor being so constructed that

- (a) the ratio of the total perforation area of each perforated plate to the reactor cross-section in the vicinity of the plate is at most 15%, preferably at most 5%, and
- (b) there is a fluid-impervious seal (as hereinbefore defined) between each perforated plate and the reactor wall and
- (c) each perforated plate is horizontal when the reaction tube is upright, and
- (d) each perforation in each perforated plate is the same size as the other perforations in that plate and the perforations are uniformly distributed over the plate, and
- (e) each perforation either has a cylindrical or bevelled inlet, or is frustoconical with a wider inlet than outlet; and
- (f) the perforated plates are evenly spaced along the reactor and the distance between each pair of adjacent perforated plates is greater than three times the diameter of the reactor,

the reactor also comprising means for passing a liquid and a gas upwards through the reactor at such a rate that return of liquid and/or gas from one of the individual reactor sections to the preceding section is substantially prevented.

When the reactor of the invention is in use, each reactor section contains a bubble bed, of which the gas hold-up increases as the height of the reactor section increases. If back-mixing of the liquid is to be completely prevented, a gas cushion that fills

the space up to the next plate is preferably formed above each bubble bed. Each of the reactor sections is, therefore, a bubble column reactor, so that the entire reactor can be called a bubble column cascade reactor.

If, by the formation of gas cushions or by a suitably chosen gas flow rate, back-mixing of the liquid or suspension through the perforations of the perforated plates is reduced to a minimum or completely prevented, then the bubble column cascade reactor of the invention exhibits the same residence time distribution as that of an ideal cascade of stirring vessels, since the gas, as well as preventing or reducing back-mixing, also causes thorough mixing of the liquid in the individual reactor sections (an ideal cascade of stirring vessels has the characteristic that in each stirring vessel there is ideal mixing of the liquid and back-mixing between the individual stirring vessels is not possible). In the reactor of the invention, a little back-mixing of the liquid or suspension through the holes in the perforated plates has no measurable influence on the residence time distribution.

As the bubble column cascade reactor of the invention functions with regard to residence time distribution in the same manner as a cascade of stirring vessels, it is possible to use the known equations (J. Kardos, *Chemische Technik*, 21st year (1969), part 4, pages 216 to 220, part 5, pages 275 to 280) for determining the mean residence time; with this mean residence time it is possible to calculate the necessary reactor capacity for a required product throughput. With the process of the invention the same residence time distribution can be obtained with considerably less technical expenditure than was necessary with previous processes. Furthermore, it is possible to obtain mean residence times of the liquid or suspension of any desired duration.

The process of the invention may be demonstrated by using a transparent model of a bubble column cascade reactor; this enables cushion formation and back-mixing to be observed. In the accompanying drawings, Figure 1 is a diagrammatic representation of a suitable reactor in the state of cushion formation, whilst Figure 2 shows a perforated plate for use in the reactor.

Referring now to the drawings, the gas flows into the reactor at (a) under the first perforated plate. Above the first perforated plate the liquid or suspension enters the reactor at (b). The perforated plates (c) are movably fixed to a central tube (d). A perforated plate having a suitable distribution of perforations is shown in Figure 2. A seal (g) between each perforated plate (c) and the inner wall of the reactor tube (e) may be formed by means of suitable material,

for example, a ring of Viton (fluoro-rubber, "Viton" is a Trade Mark) or a steel piston ring.

Above the uppermost perforated plate, the gas and the liquid or suspension are withdrawn from the reactor and passed into a separating vessel (h). The gas is returned to the reactor by a circulation pump. (k). The quantity of gas necessary for the reaction is added continuously at (l) to the circulating gas. The liquid or suspension is withdrawn at (m) from the separating vessel.

The height of the bubble bed (n) and simultaneously that of the gas cushion (o) can be adjusted by varying the volume of the gas stream (p) or the liquid stream (q).

The influence of the reactor diameter, the distance between the perforations, the number of perforations, the perforation diameter, the distribution of the perforations, the thickness of the plates and the sealing of the plates, on the one hand, and also of the volumes of the liquid and gas streams and the properties of the gas and liquid (such as density, viscosity and surface tension) on the other hand, on gas cushion formation and back-mixing of the liquid can be determined for the process of the invention.

It is found that, for a given geometry of perforated plate and reactor with a given liquid throughput, there is a characteristic gas throughput at which no back-mixing through the perforated plates occurs and a gas cushion is formed under the perforated plates. This state of flow has been called the "special flow state."

With a given perforation diameter and a given number of perforations the gas throughput required to achieve the "special flow

state" decreases as the liquid throughput increases, and simultaneously the content of liquid in the several sections increases and the thickness of the gas cushion decreases.

With the following definitions

$$Re_{Ld} = \frac{w_{Ld} \cdot d \cdot \rho_L}{\eta_L}; \quad 45$$

$$Re_{Gd} = \frac{w_{Gd} \cdot d \cdot \rho_G}{\eta_G}$$

the condition for gas cushion formation is:

$$Re_{Ld}/Re_{Gd} = 0.1.$$

In the case of gases having a very low density there is a distinct deviation from the above relation. 50

The loss of gas pressure, Δp_{total} , in the bubble column cascade reactor, for all tested pairs of substances and geometries and for all possible flow states, is represented by the following empirical relation with an error of $\pm 5\%$: 55

With the definition

$$Fr_{GD} = \frac{w_{GD}^2 \cdot \rho_G}{D \cdot g \cdot (\rho_L - \rho_G)}$$

it is, in the range $3 \cdot 10^{-7} < Fr_{GD} < 10^{-3}$, 60

$$\Delta p_{total} = \epsilon \cdot \rho_L \cdot h \cdot g \cdot n$$

The pressure loss coefficient ϵ can be determined by the following relation:

$$\epsilon = 0.31 \cdot \left(\frac{D \cdot \tau}{Fr_{GD} \cdot h} \right)^{0.2} - 0.01 \cdot \left(\frac{D \cdot \tau}{Fr_{GD} \cdot h} \right)^{0.5}$$

65 The symbols used in the above equations have the following meanings:

d perforation diameter
D reactor diameter
g acceleration due to gravity
70 h distance between perforations
n number of reactor sections
 Δp pressure loss
w velocity
 ϵ pressure loss coefficient
75 η dynamic viscosity
 ρ density
 τ relative perforation area =
 $\frac{d^2}{D^2} \times 100 \times \%$
Fr Froude number
80 Re Reynolds number
 $\%$ number of perforations in each plate

Indices:

d with reference to the perforation diameter
D with reference to the reactor diameter 85
G gas phase
L liquid

The bubble column cascade reactor of the invention and the formation of gas cushions therein were investigated first with model substances and then with chemical reactions. The results obtained are summarized in Tables 1 and 2 respectively. 90

The process of the invention can be used with special advantage for the manufacture of organo-metal compounds, especially for the manufacture of organo-aluminium compounds by the Ziegler method, in which finely divided aluminium is reacted in the presence 95

of aluminium trialkyls with hydrogen and optionally olefines.

The process of the invention may also be used for the production of aluminium trialkyls from dialkyl-aluminium hydrides and olefines.

An example of such a reaction, and of the reaction of a liquid with a gas by the process of the invention, is the manufacture of triethyl-aluminium from diethyl-aluminium hydride and ethylene. As an example of the

reaction between a liquid, a solid and a gas there may be mentioned the reaction of aluminium with triethyl-aluminium and hydrogen to form diethyl-aluminium hydride.

The "content of liquid" given in Tables 1 and 2 is the liquid content of the entire reactor multiplied by 100 and divided by the liquid and gas content of the entire reactor:

$$\text{Content of liquid} = \frac{\text{liquid content}}{\text{gas content} + \text{liquid content}} \times 100\%$$

TABLE 1

Model experiments with bubble column cascade reactors

Liquid	Liquid throughput kg/h	Gas	Gas throughput kg/h	Pressure/temperature Atm-abs./°C	Perforation- ϕ / column- ϕ mm	Free cross-section %	Mean residence time h	Column height/number of plates m/-	Content of liquid %	Gas cushion height mm
1) Dibutyl ether	21.8	Nitrogen	38.5	1/20	4/140	2.49	0.9	3/4	50	100
2) Octene	13.8	Nitrogen	17.2	1/20	2/140	1.6	1.5	3/4	57	55
3) Water	46.4	Air	35.5	1/20	4/140	2.5	0.55	3/4	50	80
4) Water	45.8	Air	14.8	1/20	2/140	1.6	0.65	3/4	59	40
5) Water	29.2	Air	12.0	1/20	4/140	1.25	1.1	3/4	66	35
6) Water a)	46.9	Air	4.0	1/20	4/140	2.5	0.93	3/4	87	0.0
" b)	"	"	11.9	"	"	"	0.7	"	65	15
" c)	"	"	19.0	"	"	"	0.62	"	58	40
" d)	"	"	33.4	"	"	"	0.51	"	48	70

TABLE 2
Examples of chemical reactions in bubble column cascade reactors

Liquid, with or without solid	Liquid throughput kg/h	Gas	Gas throughput kg/h	Pressure/ temperature Atm.abs./°C	Perfora- tion- ϕ / column- ϕ mm	Free cross- section %	Mean residence time h	Column height/ number of plates m/-	Content of liquid %	Gas cushion height mm
1) DEA	45.0	Ethylene	6.0	11/100	3/70.3	3.4	0.25	5.5/12	80	20
2) TEA and Al	45.0	Hydrogen	12.0	150/100	4.5/100	2.4	1.3	6.55/12	75	20
3) DEA	515	Ethylene	35.0	10/100	3.2/160	3.4	0.3	10/9	80	20
4) TEA and Al	505	Hydrogen	112.0	150/100	5/300	4	1.27	12/14	81	20

DEA = diethyl aluminium hydride

TEA = triethyl aluminium

The process of the invention for the re-
action of liquids with liquids in the presence
of gases and in the presence of finely divided
solids having a catalytic action can be used
with special advantage for the polymerisation
of unsaturated fatty acids with the aid of
clay catalysts. Mono- or poly-unsaturated
natural fatty acids containing 11 to 22, es-
pecially 18, carbon atoms (for example, oleic
acid, linoleic acid, linolenic acid) or mixtures
containing these acids, may be polymerised
by this method.

As catalysts there are suitable crystalline
clay minerals, especially those having a high

content of montmorillonite. Discontinuous pro-
cesses for the polymerisation of fatty acids
with clay catalysts are disclosed in German
Auslegeschriften Nos. 1,134,666 and
1,134,667. The clay minerals may be modified
by the addition thereto of alkali metal or
alkaline earth metal salts, as described in
German Auslegeschrift No. 1,280,852. The
modification of clay catalysts for the poly-
merisation of fatty acids with lithium salts
is described in German Auslegeschriften Nos.
1,443,938 and 1,443,968.

Temperatures between 200 and 280°C are
suitable for the continuous polymerisation of

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- 5 fatty acids in accordance with the invention. In order to avoid decarboxylation of the fatty acid(s) at elevated temperatures, it is advantageous to carry out the reaction in the presence of 1 to 5% of water calculated on the weight of the fatty acid(s).
 10 The reaction is preferably carried out under super-atmospheric pressure. It is possible to carry out the reaction without the application of pressure, an appropriate quantity of water vapour being added to the inert gas, which is preferably nitrogen.
- 15 When the process of the invention is applied to the polymerisation of fatty acids, the economies which usually result from continuous operation are obtained. An additional advantage is that the flow of gas causes purification of the product, and this has an effect on the initial odour of any resin subsequently produced therefrom.
 20 The results obtained in three polymerisation reactions using the process of the invention are given in Table 3.

TABLE 3

Examples with chemical reactions in bubble column cascade reactors

Liquid	Solid	Throughputs of liquid and solid kg/h	Gas	Gas throughput kg/h	Pressure/temperature Atm.abs./°C	Perforation- ϕ / column- ϕ mm	Free cross-section %	Mean residence time h	Column height/number of plates m/-	Yield of polymerized fatty acid %
1) FTS	BCX	38 3.8	Nitrogen	13	5/250	4/150	4	1.5	7.6/11	48
2) FTS	BCX	38 3.8	steam	10	6/250	4/150	4	1.5	7.6/11	67
3) FTS	BCX	38 3.8	steam	10	1/250	4/150	4	1.5	7.6/11	64

BCX = clay catalyst

FTS = tall oil fatty acid

WHAT WE CLAIM IS:—

1. A continuous process for carrying out a physical or chemical reaction which process comprises passing a liquid and a gas upwards through a reactor which includes a number of perforated plates, which plates are positioned across the direction of flow of the liquid and gas and divide the reactor into a number of individual sections, the reactor being so constructed that
 - (a) the ratio of the total perforation area of each perforated plate to the reactor cross-section in the vicinity of that plate is at most 15%, and
 - (b) there is a fluid-impervious seal (as hereinafter defined) between each perforated plate and the reactor wall, and
 - (c) each perforated plate is horizontal, and
 - (d) each perforation in each perforated plate is the same size as the other perforations in that plate and the perforations are uniformly distributed over the plate, and
 - (e) each perforation either has a cylindrical or bevelled inlet, or is frustoconical with a wider inlet than outlet, and
 - (f) the perforated plates are evenly spaced along the reactor and the distance between each pair of adjacent perforated plates is greater than three times the diameter of the reactor,
 and the rates of flow of the liquid and the gas through the reactor being such that return of liquid and/or gas from one of the individual reactor sections to the preceding section is substantially prevented.
2. A process as claimed in claim 1, wherein the ratio of the total perforation area of each perforated plate to the reactor cross-section is at most 5%.
3. A process as claimed in claim 1 or claim 2, wherein the return of liquid and gas from one individual reactor section to the preceding section is completely prevented.
4. A process as claimed in claim 1 or claim 2, wherein the rates of flow of the liquid and gas are such that a gas cushion is formed below each perforated plate.
5. A process as claimed in any one of claims 1 to 4, wherein the liquid reacts with the gas.
6. A process as claimed in claim 5, wherein the liquid is diethylaluminium hydride and the gas is ethylene.
7. A process as claimed in any one of claims 1 to 4, wherein the liquid comprises two different chemical substances, each of which is in the liquid phase, and these two substances react together in the presence of the gas.
8. A process as claimed in any one of claims 1 to 4, wherein the liquid carries along with it a finely divided solid.
9. A process as claimed in claim 8, wherein the proportion of finely divided solid is at most 15% by weight, calculated on the weight of the liquid.
10. A process as claimed in claim 8 or claim 9, wherein the liquid reacts with the solid in the presence of the gas.
11. A process as claimed in claim 8 or claim 9, wherein the liquid reacts with the solid and with the gas.
12. A process as claimed in claim 11, wherein the liquid is a trialkyl-aluminium, the gas is hydrogen, and the solid is aluminium.
13. A process as claimed in claim 8, wherein the finely divided solid acts as a catalyst for the chemical reaction.
14. A process as claimed in claim 13, wherein the proportion of the finely divided solid is at most 20% by weight, calculated on the weight of the liquid.
15. A process as claimed in claim 13 or claim 14, wherein the liquid comprises two different chemical substances, each of which is in the liquid phase and which can react together in the presence of the gas and the finely divided solid, or the liquid comprises a single substance which can polymerise in the presence of the gas and the finely divided solid.
16. A process as claimed in claim 15, wherein the liquid comprises one or more unsaturated fatty acids and the solid comprises a clay catalyst.
17. A process as claimed in claim 16, wherein the or each acid is a mono- or polyunsaturated natural fatty acid containing 11 to 22 carbon atoms.
18. A process as claimed in claim 16 or claim 17, wherein the clay catalyst is a clay mineral modified by the addition thereto of an alkali metal or alkaline earth metal salt.
19. A process as claimed in any one of claims 16 to 18, which is carried out at a temperature of from 200 to 280°C.
20. A process as claimed in any one of claims 16 to 19, which is carried out in the presence of 1 to 5% of water, calculated on the weight of the fatty acid(s).
21. A process as claimed in any one of claims 16 to 20, which is carried out at a pressure greater than atmospheric pressure.
22. A process as claimed in claim 1, carried out substantially as described herein with reference to, and as illustrated by, the accompanying drawings.
23. A process as claimed in claim 1, carried out under the conditions specified in Table 1.
24. A process as claimed in claim 1, carried out substantially as described in Table 2 or Table 3.
25. A reactor for carrying out the process of claim 1, which reactor comprises a reaction tube and a number of perforated plates positioned across the tube to divide the tube into

- a number of individual sections, the reactor being so constructed that
- 5 (a) the ratio of the total perforation area of each perforated plate to the reactor cross-section in the vicinity of that plate is at most 15%, and
- (b) there is a fluid-impervious seal (as hereinbefore defined) between each perforated plate and the reactor wall, and
- 10 (c) each perforated plate is horizontal when the reaction tube is upright, and
- (d) each perforation in each perforated plate is the same size as the other perforations in that plate and the perforations are uniformly distributed over the plate, and
- 15 (e) each perforation either has a cylindrical or bevelled inlet, or is frustoconical with a wider inlet than outlet, and
- 20 (f) the perforated plates are evenly spaced along the reactor and the distance between each pair of adjacent perforated plates is greater than three times the diameter of the reactor,
- the reactor also comprising means for passing a liquid and a gas upwards through the reactor at such a rate that return of liquid and/or gas from one of the individual reactor sections to the preceding section is substantially prevented.
- 25 26. A reactor as claimed in claim 25, wherein the ratio of the total perforation area of each perforated plate to the reactor cross-section is at most 5%.
- 30 27. A reactor as claimed in claim 25, constructed substantially as described herein with reference to, and as illustrated by, the accompanying drawings.
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COMPLETE SPECIFICATION

1 SHEET

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